Isothermal Molecular Weight Determination: Apparatus, Procedure, and Study of Effect of Solvent and Standard on Accuracy and Precision

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A study was made of the isothermal molecular weight determination; the apparatus constructed and the procedure developed are described. An extensive investigation was carried out to provide reliable guides for the selection of the correct solvents and standard reference compounds to be used in the molecular weight determination. This study produced statistical evidence of the behavior, in five different solvents, of representative compounds from each of the following chemical groups: hydrocarbons, alcohols, ketones, esters, ethers, acids, nitriles, amines, and sulfides.

Analysis showed that acetone and ethyl acetate are the best solvents if the composition of the sample is not known. Chloroform proved to be a good solvent except for samples in which hydrogen bonding could occur. *n*-Heptane was satisfactory for six of the eight types of compounds; benzene was by far the poorest solvent.

In addition to the isothermal determination of number-average molecular weight, other methods include the cryoscopic, ebullioscopic, gas density, and osmotic pressure procedures. The most popular and reliable method for the lower molecular weight range is the isothermal system.

The various methods, types of apparatus, laws, and conceptions basic to this work have been detailed previously (1–13). Briefly stated, a thermal transformation (the necessary antecedent of a difference in the rate of condensation on and evaporation from a drop of solution) is sensed by a thermistor assembly in the solvent-saturated vapor chamber of a thermostated system. This temperature change is relayed as resistance by a Wheatsone bridge circuit and, via a voltage divider, is finally recorded on a strip chart. The change in resistance (ΔR), thus measured, is used to calculate the molecular weight.

For this determination an apparatus was assembled from commercially available and modified equipment. After our apparatus was put in use, it immediately became apparent that a detailed chemical and statistical behavior study, employing certain solvents, of specific types of chemical compounds (samples and standards) was required to provide a dependable guide for future analysis.

METHOD

Apparatus

The molecular weight apparatus is shown in Fig. 1. Figure 2 shows the vapor chamber assembly (without glass jar) in detail.

(a) *Vapor chamber.* — Manufactured by Arthur H. Thomas Co.[2] The chamber head, which is a solid block of brass plated with nickel, contains four sockets. The large center socket holds the thermistor assembly and the three side sockets hold syringes. A stainless steel tube, which supports a small funnel, protrudes through a small hole in the top of the block. The vapor chamber itself consists of a glass jar compressed by a threaded clamping frame against a Teflon-covered rubber gasket that rims the inside of the chamber head. Within the vapor chamber a paper lining is held erect by a stainless steel screen.

For more efficient sealing against water vapor, the top of the chamber jar was ground just enough to give a very flat surface and the base of the clamping frame was replaced by a metal disk on whose surface was cemented a rubber ring with outside diameter slightly larger than that of the jar.

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[2] Mention of company or trade names does not imply endorsement by the Department of Agriculture over others not named.

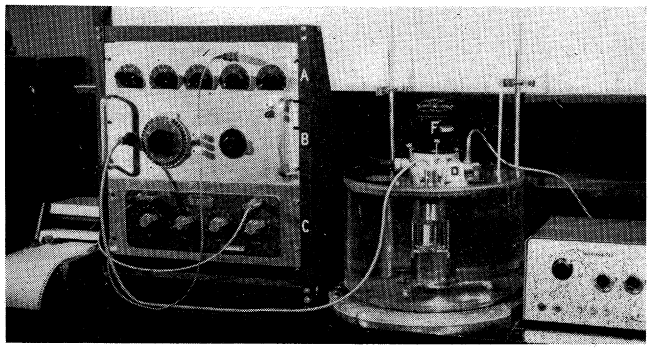

Fig. 1.—**Molecular weight apparatus: Varian recorder, (A and B) Wheatsone bridge, (C) voltage divider, (D) bath cover, (F) Sargent bath motor with stirrer and heat assembly.**

(b) *Syringes.*—Fischer and Porter Co. These are a new, improved, Lauer-tipped, pipet control type, in which a Teflon plunger on a threaded stainless steel rod moves through a threaded plastic cap.

(c) *Constant temperature water bath assembly.*—The water temperature was controlled to ± 0.003°C through a Sargent Thermonitor Model SW (Sargent Cat. No. S-82055), with a cable thermistor (Sargent Model No. S-81645), and a heater and circulator for thermostatic baths (Sargent Model No. 4733). The noninsulated Pyrex glass container was fitted with a bath cover which supports the two vapor chamber units, a syringe holder, and two sample support units.

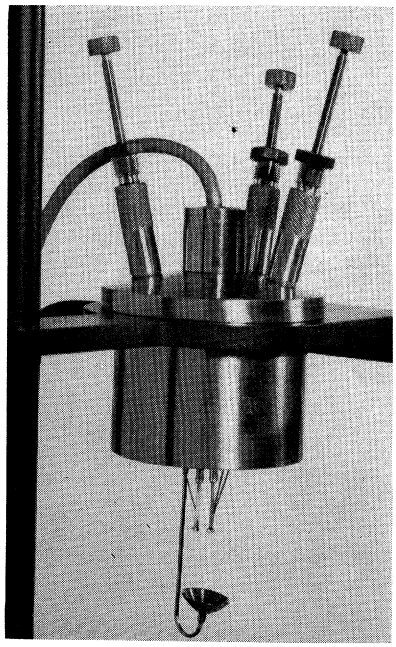

Fig. 2.—**Thermistors, Fischer and Porter syringes, and A. H. Thomas vapor chamber assembly head.**

(d) *Wheatstone bridge* (5, 10).—The settings on the far right dial shown in Fig. 1 (B) are for the following measurements: *2*, the resistance of the sensing thermistor; *3*, the resistance of the reference thermistor; *4*, the value of an unknown external resistance; and *5*, the ΔR measurement (sensing thermistor change versus reference thermistor).

(e) *Recorder.* — Varian Associates graphic recorder, range 1 mv to 1 v, Model G14.

(f) *Thermistors.*—100 K ohms at 25°C matched from 0.25 to 1%. The thermistors used in this study were purchased as unbeaded individual thermistors from Fenwall Electronics, Inc., No. Ga51P8. They were then matched, beaded at the tips with lead glass (Corning Stock No. 200129) in this laboratory, and mounted. They were preferably of uneven length and the longer (sensing) thermistor was approximately 0.5 cm shorter (about 0.9 cm from the cup) than that from A. H. Thomas. Their greater distance from the metal cup allowed many successive determinations to be made without emptying the cup and therefore without disturbing the vapor chamber equilibrium.

Procedure

Assembly of vapor chamber unit.—Mount the paper lining around its metal support and place it in the chamber jar. Place the Teflon gasket in the base of the chamber head and clamp the jar against the gasket. Place approximately 30 ml pure solvent in the chamber. (*Caution:* This should bring the solvent almost up to the point of the junction between the

stainless steel funnel and its supporting tube and should saturate the paper lining. The metal cup should be filled.)

Place the thermistor assembly and 3 syringes in their vapor chamber sockets. For optimum conditions, let both the water bath and the vapor chamber stand overnight to come to equilibrium (± 0.001°C in vapor chamber air). During molecular weight determinations, equilibrate syringes in the rack suspended in the water bath before drawing solution into them.

Determination.—Fill 2 equilibrated syringes with solvent and place them in their chamber sockets. Place an empty syringe in the sample socket. Let them equilibrate at least 15 min. Rinse both thermistors with 5 drops of solvent and equilibrate chamber assembly one-half hour.

Turn on recorder, using the slow speed and the 1 mv range. The bridge dial is set to read ΔR (Fig. 1 (B); far right dial set at 5). When necessary, balance the bridge by adjusting the potentiometer dial (Fig. 1 (B), far left) to bring the recorder near zero when pure solvent is on both thermistors. Set the voltage divider Fig. 1 (C)) at a place dictated by sample concentration (ideally at 5 on the far left dial for a 50% signal reception).

Prepare a solution of the standard reference compound (1 ml minimum, 5 ml optimum) whose mole fraction range is 0.002–0.004. Record both the standard and solvent weights. Rinse an equilibrated syringe approximately 3 times with standard sample solution, fill with about 0.5 ml solution, and place in the chamber socket, allowing 15 min for equilibration.

Rinse sample thermistor with 5 drops of solvent. After 8 min, note the bridge imbalance as recorded on the chart paper. This is the blank.

Immediately rinse the sample thermistor with 5 drops of standard solution. Wait 8 min and again note the bridge imbalance. This is the total ΔR. Subtract the blank from this reading to obtain the ΔR of the standard. Repeat rinsings with solvent and standard solution alternately to obtain two more blanks and two more total ΔR readings. Average the last two results (ΔR − blank) and calculate the K factor, using this average figure.

Rinse and fill an equilibrated syringe with the unknown sample solution whose sample and solvent weights have been recorded. Replace the standard solution syringe in the vapor chamber with one containing sample solution. Allow it to equilibrate 15 min. Then follow the same procedure used with the standard solution and calculate the molecular weight.

Calculations:

Mole fraction of standard = moles std/(moles std + moles solvent)

K = ΔR std/mole fraction of std

Molecular weight = [g unknown (mol. wt solvent)/g solvent] × [(K/ΔR unknown) − 1]

Adaptation of procedure to different types of solvents.—Solvents differ in sensitivity and in the rate of attaining steady-state temperature. However, they may be divided into two general groups: Group I: chloroform, methylene chloride, carbon tetrachloride, *n*-heptane, methyl ethyl ketone, benzene, ethyl acetate, acetone, and dioxane; Group II: isopropyl alcohol, ethanol, and water. Higher temperatures (37°C minimum), longer equilibrium times (20 min minimum), and additional drops of rinse solution must be used for the Group II solvents. The slope of the calibration curve for these solvents is generally greater.

If the temperature is too low for the individual solvent, not enough solvent will be present in the vapor state. On the other hand, thermal gradients capable of affecting results may be present in the cell if the temperature is too high. For ± 1% accuracy, daily determination of the calibration constant K was necessary. For ± 4% accuracy, a calibration curve can be made for each solvent and the curve used, as long as the same thermistors are in the system and the temperature is not changed.

Summary of the salient elements of the procedure

1. Water bath temperature:
   Group I solvents, 35°C
   Group II solvents, 37°C minimum
2. Concentration range: 0.002–0.004 mole fractions
3. Recorder settings: range 1 mv, chart speed 2″/hr.
4. Equilibration time preliminary to sample run (sample syringe in vapor chamber):
   Group I solvents, 15 min
   Group II solvents, 20–30 min
5. Number of drops of sample used to rinse thermistors:
   Group I solvents, 5 drops (approximately 0.1 ml sample)
   Group II solvents, 6–10 drops
6. Equilibration time after sample addition to thermistors:

Group I solvents, 8 min
Group II solvents, 20–30 min

7. ΔR readings: three obtained on each solution.
8. Reference thermistor: not rinsed between runs.
9. Reference compound: either benzil or a compound of molecular weight and chemical structure similar to that of the unknown.

Results and Discussion

Basic Characteristics and Parameters

In this differential system, matched thermistors respond satisfactorily to very small temperature changes, using voltages that are suitably efficient but small enough to keep the thermistors within the linear portion of their volt-ampere curve and to minimize the effect of self heating. Shifting of minute temperature gradients in the chamber affects the stability of the system. Therefore, the external environment of the vapor chamber must be maintained at a constant temperature (± 0.003°C maximum variation). To this end, a water bath producing symmetrical heating with relatively vibration-free stirring and a low energy input control system was used. The apparatus area was free of drafts and physical vibration, with constant temperature and humidity. A voltage regulator was used to minimize the effect of variation in line voltage.

A solvent (certified 99 mole % pure or ACS grade having < 0.3% moisture content) covers the bottom of the vapor chamber, fills the metal cup, and saturates the metal-supported paper lining, causing the chamber atmosphere around the thermistors to become saturated with solvent vapor. This is a fundamental requirement for the stability and proportionality of the determination since the temperature change of the sample solution on the thermistor is caused by a difference in rate of condensation and evaporation of solvent vapor on the solution drop. Although the solvent in the vapor chamber and its cup becomes increasingly contaminated with solute during the analysis, no significant error is produced because the thermistors are at least 0.5 cm above the chamber cup. The solute contamination of the solvent held by the paper lining above the liquid level in the chamber is insignificant.

The flattened glass bead attached to the thermistor tip increases and helps to regulate drop size. This leads to a more stable and reproducible response. When a drop is put on the thermistor, the equilibrium of the system is momentarily disturbed, but a constant number of drops are applied, which causes a similar disturbance, thus permitting precise and accurate ΔR values to be obtained. Therefore, a constant flow technique was not necessary. There was no need for a factor to correct for heat loss from the solution drop by conduction along the thermistor or by radiation. Any small resultant lowering of the signal magnitude from these effects was constant throughout the determination. Variation in amount of light striking the thermistors can affect the results adversely. The temperature equilibrium in the chamber is affected when the water level in the bath is not maintained so that the water touches the top of the panel which supports the cell and syringe holder.

Finally, the steady-state response was never reached or erroneous values were obtained if (*1*) the temperature of the sample and the solvent rinse solution differed from the cell temperature, (*2*) the solute exerted its own vapor pressure, (*3*) solvents had volatile impurities, or (*4*) excess water vapor entered the vapor chamber.

Statistical Analysis of Results

Compounds were used whose structures generally illustrated the various basic types (hydrocarbons, alcohols, ketones, esters, ethers, acids, nitriles, amines, and sulfides) routinely analyzed in this laboratory. All samples were at least 99.5% pure based on elemental analysis or manufacturer's certification. The solvents used were low boiling at an optimum of 50–100°C (chloroform, *n*-heptane, benzene, ethyl acetate, and acetone).

Six separate analyses were made on each sample and the values obtained were used to calculate each mean, standard deviation, and "t" value recorded in Tables 1–11. The

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Table 1. The isothermal molecular weight determination of the alkane, octadecane, in various solvents, using benzil as standard

Solvent	Molecular Weight		Std Dev.	*t* Value[a]
	Theory	Mean		
Acetone	254	253	1.63	1.00
Chloroform	254	254	0.84	−1.46
Ethyl acetate	254	254	1.10	0.00
Benzene	254	253	2.73	−0.60
n-Heptane	254	254	1.17	0.35

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

statistical results obtained are summarized in Tables 12 and 13.

The statistical results show that all compounds can be analyzed without regard to functional groups if ethyl acetate is the solvent when benzil is the standard. Therefore, when a compound's structure is unknown, a test for solubility in ethyl acetate should be performed. Acetone is the second best solvent. Benzene proved to be the poorest, being unsatisfactory for four of the eight

Table 2. The isothermal molecular weight determination of two esters, using various solvents and standards

Solvent	Compound	Standard	Molecular Weight		Std Dev.	*t* Value[a]
			Theory	Mean		
Acetone	*n*-Heptyl stearate	Benzil	383	383	2.37	0.00
Acetone	*n*-Heptyl stearate	Ethyl laurate	383	383	1.05	0.54
Chloroform	Ethyl laurate	Benzil	228	228	1.76	0.00
Ethyl acetate	Ethyl laurate	Benzil	228	228	0.82	−1.00
Benzene	Ethyl laurate	Benzil	228	229	1.72	1.18
n-Heptane	Ethyl laurate	Benzil	228	216	1.17	−24.79
n-Heptane	Ethyl laurate	Octadecane	228	228	1.17	0.35

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 3. The isothermal molecular weight determination of *n*-octyl ether in various solvents, using benzil and di-*n*-decyl ether as standards

Solvent	Standard	Molecular Weight		Std Dev.	*t* Value[a]
		Theory	Mean		
Acetone	Benzil	242	241	1.33	−1.54
Acetone	Di-*n*-decyl ether	242	242	1.33	−0.31
Chloroform	Benzil	242	243	1.10	2.24
Ethyl acetate	Benzil	242	242	0.75	0.54
Benzene	Benzil	242	254	1.17	25.49
Benzene	Di-*n*-decyl ether	242	241	0.82	−2.00
n-Heptane	Benzil	242	242	1.47	−0.28

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 4. The isothermal molecular weight determination of two ketones, using various solvents and standards

Solvent	Compound	Standard	Molecular Weight		Std Dev.	*t* Value
			Theory	Mean		
Acetone	Methyl pentadecyl ketone	Benzil	248	250	0.75	7.05
Acetone	Methyl pentadecyl ketone	Methyl heptadecyl ketone	248	249	0.98	2.08
Chloroform	Methyl nonyl ketone	Benzil	170	171	0.75	2.71
Ethyl acetate	Methyl pentadecyl ketone	Benzil	248	249	2.90	0.84
Benzene	Methyl pentadecyl ketone	Benzil	248	263	0.82	43.99
Benzene	Methyl pentadecyl ketone	Methyl nonyl ketone	248	249	0.82	2.00
n-Heptane	Methyl pentadecyl ketone	Benzil	248	247	1.21	−1.35

types of compounds tested (ethers, ketones, alcohols, and acids).

When the functional groups of the samples are known, solvents may be chosen selectively by using the statistical results obtained. The molecular weights of alkanes

Table 5. The isothermal molecular weight determination of two nitriles in various solvents, using benzil as standard

Solvent	Compound	Molecular Weight		Std Dev.	*t* Value
		Theory	Mean		
Acetone	Lauronitrile	181	181	1.37	0.60
Chloroform	Lauronitrile	181	182	0.84	1.46
Ethyl acetate	Lauronitrile	181	181	0.82	1.00
Benzene	Lauronitrile	181	181	1.50	0.54
n-Heptane	Stearonitrile	265	265	1.17	−0.35

Table 6. The isothermal molecular weight determination of two alcohols, using various solvents and standards

Solvent	Compound	Standard	Molecular Weight		Std Dev.	*t* Value[a]
			Theory	Mean		
Acetone	Tetradecanol	Benzil	214	215	0.78	2.91
Acetone	Tetradecanol	Octadecanol	214	215	0.75	3.80
Chloroform	Octadecanol	Benzil	270	273	1.21	5.39
Chloroform	Octadecanol	Tetradecanol	270	271	1.03	1.58
Ethyl acetate	Octadecanol	Benzil	270	271	1.75	1.86
Benzene	Tetradecanol	Benzil	214	222	1.86	10.96
Benzene	Tetradecanol	Cetyl alcohol	214	214	1.37	0.60
n-Heptane	Octadecanol	Benzil	270	269	1.17	−2.44

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 7. The isothermal molecular weight determination of two organic acids, using various solvents and standards

Solvent	Compound	Standard	Molecular Weight		Std Dev.	*t* Value[a]
			Theory	Mean		
Acetone	Palmitic acid	Benzil	256	258	0.82	7.00
Acetone	Palmitic acid	Anisic acid	256	257	1.10	2.24
Chloroform	Palmitic acid	Benzil	256	328	18.04	9.75
Chloroform	Benzoic acid	Anisic acid	122	122	0.52	1.58
Ethyl acetate	Palmitic acid	Benzil	256	254	2.58	−1.58
Benzene	Palmitic acid	Benzil	256	437	0.82	543.89
Benzene	Palmitic acid	Stearic acid	256	256	0.75	0.54
n-Heptane	Palmitic acid	Benzil	256	482	22.37	24.80
n-Heptane	Palmitic acid	Stearic acid	256	256	0.89	0.00

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 8. The isothermal molecular weight determination of two amines, using various solvents and standards

Solvent	Compound	Standard	Molecular Weight		Std Dev.	*t* Value[a]
			Theory	Mean		
Acetone	Hexadecylamine	Benzil	241	252	1.84	14.67
Acetone	Hexadecylamine	Octadecylamine	241	241	0.75	0.00
Chloroform	Hexadecylamine	Benzil	241	240	1.76	−0.70
Chloroform	Octadecylamine	Hexadecylamine	270	269	1.33	−1.54
Ethyl acetate	Hexadecylamine	Benzil	241	242	2.14	0.95
Benzene	Hexadecylamine	Benzil	241	252	0.75	35.24
Benzene	Hexadecylamine	Octadecylamine	241	241	0.52	1.58
n-Heptane	Hexadecylamine	Benzil	241	241	1.32	0.31

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

and nitriles were determined satisfactorily with benzil as standard in all of the solvents studied. Benzil can be used as a standard for (*1*) esters in all solvents except *n*-heptane, (*2*) ethers and ketones in all solvents except benzene, (*3*) alcohols in all solvents except chloroform and benzene, (*4*) acids in ethyl acetate and acetone only, (*5*) amines in all solvents except acetone and benzene, and (*6*) sulfides in acetone. Reference standards having functional groups similar to the sample must be substituted for benzil in the case of the solvents listed here as exceptions.

The molecular weight of compounds (up to 10,000) can be determined with less than 2% error. Within this range of error, the standard deviations and "t" values increase slightly with an increase in the magnitude of individual molecular weights.

Table 9. The isothermal molecular weight determination of an organic sulfide, dodecyldisulfide, in acetone

Standard	Molecular Weight		Std Dev.	*t* Value[a]
	Theory	Mean		
Octadecane	403	401	2.449	2.00
Ethyl laurate	403	403	3.386	0.24

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 10. Effect of difference between molecular weights of the compound and its standard on the isothermal molecular weight determination, using acetone as solvent

Compound	Std Mol. Wt.	Standard	Molecular Weight		Std Dev.	*t* Value[a]
			Theory	Mean		
Octadecane	212	Eicosane	254	255	0.89	2.74
Octadecane	228	Ethyl laurate	254	255	0.82	2.00
Octadecane	383	*n*-Heptyl stearate	254	255	0.98	2.90
Methyl pentadecyl ketone	170	Methyl nonyl ketone	248	249	0.89	2.74
Methyl pentadecyl ketone	274	Methyl heptadecyl ketone	248	249	0.98	2.08

[a] Critical $t_{0.05} = 2.571$; $n = 6$.

Table 11. Isothermal molecular weight determination of higher molecular weight compounds, using benzil as standard

Solvent	Compound	Molecular Weight		Std Dev.	*t* Value[a]
		Theory	Mean		
Chloroform	Tristearin	891	896	10.74	1.10
Chloroform	Ethyl laurate	228	228	1.10	0.00
Benzene	Tristearin	891	897	9.92	1.44
Benzene	Ethyl laurate	228	228	1.17	0.35
Benzene	Polystyrene	10,300	10,167[b]	—	—

[a] Critical $t_{0.05} = 2.571$; $n = 6$.
[b] Av. of 2 values.

Table 12. Summary of statistical results obtained in the molecular weight determinations—precision (standard deviation)

Type of Sample	Av. *s*	Acetone	Chloroform	Ethyl Acetate	Benzene	*n*-Heptane
Alcohols	1.21	0.75	1.03[a]	1.75	1.37	1.17
Acids	1.16	1.10[a]	0.52[a]	2.58	0.75	0.89[a]
Ethers	1.13	1.33	1.10	0.75	0.82[a]	1.47
Ketones	1.34	0.98[a]	0.75	2.90	0.82[a]	1.21
Nitriles	1.14	1.37	0.84	0.82	1.50	1.17
Alkanes	1.43	1.63	0.84	1.10	2.73	1.17
Esters	1.57	2.37	1.76	0.82	1.72	1.17[a]
Amines	1.30	0.75[a]	1.76	2.14	0.52[a]	1.32
Overall av., *s*	1.28	1.28	1.08	1.63	1.27	1.20

[a] Results obtained with a similar standard.

Table 13. Mean deviations[a] from the theoretical molecular weight

Type of Sample	Solvent				
	Acetone	Chloroform	Ethyl Acetate	Benzene	*n*-Heptane
Alcohols	1.17	2.67	1.67	8.33	1.17
Acids	2.33	71.83	2.33	180.67	226.50
Ethers	1.17	1.00	0.66	12.17	1.17
Ketones	2.17	0.83	2.67	14.67	1.00
Nitriles	1.00	0.83	0.67	1.00	0.83
Alkanes	1.33	0.83	0.67	2.00	0.83
Esters	2.00	0.50	0.67	1.50	11.83
Amines	11.16	1.50	1.83	10.83	1.17
Av. mol. wt dev.	2.79	10.00	1.40	28.90	30.56

[a] Benzil is used as standard for all compounds, as would be done if the classification of the sample were unknown.

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